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New high-pressure systems to investigate clathrate hydrates stability and role in volatile outgassing on Titan and Enceladus

M. Choukroun (1), M.B. Barmatz (1), O. Grasset (2), R.P. Hodyss (1), E. Le Menn (2), W.D Smythe (1), G. Tobie (2).
(1) Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA (Mathieu.Choukroun@jpl.nasa.gov).
(2) UMR-CNRS 6112 – Planétologie et Géodynamique, Université de Nantes, Nantes, France.

Abstract

The origin of Titan's atmospheric methane and of the volatiles measured in Enceladus' south pole plumes remain, to this day, unresolved. Clathrate hydrates are among the favored deep-seated reservoir candidates. However, the conditions allowing for their dissociation and the release of volatiles to the atmosphere (Titan) or the plumes (Enceladus) are still poorly constrained. This is mainly because there is a lack of knowledge on the stability of mixed clathrate hydrates in presence of anti-freeze agents such as ammonia. We present two new high-pressure systems, a high-pressure cryogenic calorimeter and a fluid pressure optical cell, currently being developed at JPL and the Laboratoire de Planétologie et Géodynamique de Nantes, respectively, that are designed to address this deficiency in the literature. Preliminary results from these studies will be shown.

1. Introduction

Titan: The Gas Chromatograph and Mass Spectrometer (GCMS) instrument onboard the Huygens probe [1] has measured 1.4-5% CH_4 in Titan's thick N_2 atmosphere. Photochemical models indicate that this compound would disappear in less than 100 My [2], implying the existence of replenishment processes. Hydrocarbon lakes do exist on Titan's surface, but their estimated volume [3] cannot account for this replenishment on geologic timescales. An internal reservoir of methane, such as a deep-seated layer of methane clathrates [4], could be the source of atmospheric replenishment via cryovolcanic events. However, such events require a complex geologic setting [5], and better constraints on the effect of anti-freeze agents like NH_3 on the stability of clathrates in the subsurface (0-10 km) environment of Titan.

Enceladus: The small fractions of CO_2 and NH_3 detected by the Ion Neutral Mass Spectrometer (INMS) onboard the Cassini spacecraft [6] in Enceladus' south pole plumes have been interpreted as having a geyser-like eruptive origin. Other hypotheses involve the destabilization of clathrate hydrates at depth [7], and the sublimation of water ice along with impurities from the icy shell. As in the case of Titan, better constraints on the stability of clathrate hydrates in the presence of ammonia, at conditions of the subsurface of Enceladus are needed to better understand the origin of the south pole plumes volatiles.

Our ultimate objective is to conduct such measurements to better model exchange processes on these two Saturnian moons. The development of new facilities capable of making these measurements is a necessary first step to accomplish this goal.

2. Experimental setups

2.1 High-pressure cryogenic calorimeter

We use a liquid nitrogen – cooled Setaram BT2.15 calorimeter, located at the Ice Physics Laboratory, JPL (see Figure 1). The temperature range achievable with this instrument is 77-473 K. This calorimeter uses Calvet elements (3D arrays of thermocouples), to measure the heat flux required to follow a predefined heating rate within a sample and a reference cell with a resolution of 0.1 μW.

A high-pressure system is being implemented in order to develop the capability of investigating the pressure range 0-100 bars. This system includes: high-pressure cells with a gas flow system (from Setaram), a gas handling system to deliver the gas from 1K bottles of CH_4, CO_2, and N_2, a vacuum system, and a vent system.

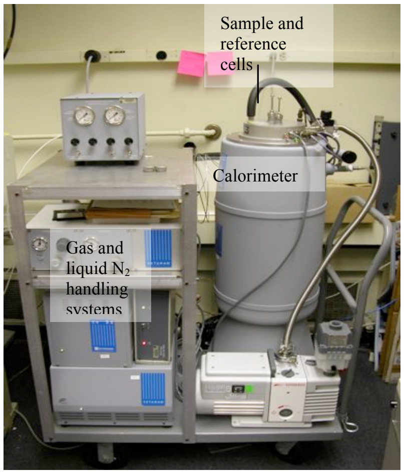

Figure 1: Photograph of the Setaram BT2.15 Calvet calorimeter.

2.2 Fluid pressure optical cell

A hydraulic pressure cell with a large, 1 mm^3 sample volume has been developed at the Laboratoire de Planétologie et Géodynamique de Nantes (see Figure 2). Cooling and heating are provided by Peltier elements, within the range 240-310 K. The hydraulic fluid of choice is compressed by a manual generator to achieve up to 2500 bars. Sapphire windows allow optical access to the samples, for microscopy, Raman and InfraRed spectroscopy.

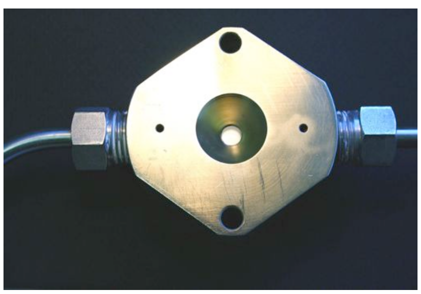

Figure 2. Photograph of the fluid pressure cell.

The pressure generation system is being modified, with the addition of a separating piston and corrosion-resistant coating to provide a chemical compatibility with ammonia.

3. Measurements - conclusions

With the calorimeter, clathrate hydrates will be synthesized within the cells from an H_2O-NH_3 aqueous solution. Then, cooling and heating tests will be conducted for several gas pressures in order to measure simultaneously the dissociation curve and thermodynamic properties (heat capacity, latent heat).

Similarly, clathrate hydrates will be synthesized from the solution of interest within the fluid pressure cell. Dissociation curves will be measured by varying temperature, and following optically and via Raman and diffuse reflectance infrared spectroscopy the samples' evolution.

We are nearing the end of the development phase for both apparatus, and will present preliminary tests and results at the meeting.

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